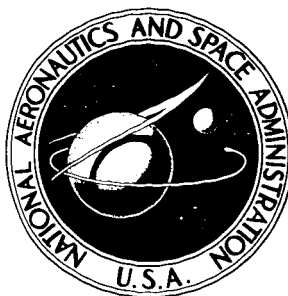


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**INSTANTANEOUS MONITORING OF
MULTICOMPONENT EXPIRED GASES**

by A. E. Barrington

Prepared by

GCA CORPORATION

Bedford, Mass.

for Flight Research Center

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EXPIRED GASES

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INSTANTANEOUS MONITORING OF MULTICOMPONENT EXPIRED GASES

by A.E. Barrington

The analysis of expired multicomponent gases is of great physiological interest. If available rapidly and reliably it can contribute significantly in the evaluation of the effects of space flight on the biological functions of man.

Because of the urgent requirements of the manned space flight program, the prototype gas analyzers described below were developed specifically for aerospace applications. Their design thus inevitably was subject to restrictions of weight, volume and power consumption. Nevertheless, their operational performance has been most encouraging. Since environmental restrictions would be far less severe in a terrestrial medical facility, one can readily envisage a scaled-up, yet portable, rugged gas analyzer optimized for prolonged, continuous and reliable service. Because the read-out is directly obtained in the form of electrical signals, modern data-handling methods can readily be used. For example, a fully computerized unit could be devised for the automatic control of vital physiological processes in operating rooms and for other types of emergency treatment.

The sensing element of the gas analyzer is called a mass spectrometer whose concept utilizes two basic physical phenomena: first, gaseous atoms and molecules can readily be charged electrically; second, there is a selective effect by electric and magnetic forces on such charged particles which depends on the atomic or molecular mass.

The manner in which charged atoms and molecules are produced can best be understood by considering the nature of matter in general. Under suitable conditions, it is possible to release electrons, very light particles carrying a negative electrical charge from every known substance, solid, liquid or gas under suitable conditions. An electron obtained from any one material is identical with electrons obtained from any other material. But since matter is electrically neutral, matter must also consist of positive charges in order to neutralize the negative charge of the electron. The simplest neutral particle of a given substance is an atom; molecules may consist of one, two or more atoms. All of the positive charge associated with an atom is concentrated within a very small core, called the nucleus. The nucleus accounts for almost the entire mass of the atom and the mass differs for atoms of different chemical elements. The nucleus is surrounded by electrons whose number depends on the particular chemical element; for the naturally occurring elements, it varies from 1 hydrogen to 92 for uranium. The electrons move in orbits at various distances about the nucleus. The outermost electrons are easily removed from the atom. Molecules consist of one or more nuclei, held characteristic distances apart, the entire configuration being surrounded by orbiting electrons contributed by individual component atoms.

By detaching one or more electrons from a neutral particle, a positive molecular or atomic ion is produced. The positive charge remaining on the particle is equal to the negative charge thus removed. Since the electronic

negative charge is constant, the positive charge is always a whole multiple of this quantity. In the simplest case, we shall be concerned with singly-charged, positive ions, which have been stripped of only one electron.

The purpose of the mass spectrometer is the determination of the percentage abundance of ions of different atomic or molecular species corresponding to the component gases of a given gas mixture. The first step in this process is the production of an adequate number of positive ions. One of the most efficient processes of ion production is the bombardment of gas molecules by a stream of high-speed electrons. As in many types of electronic devices, electrons are conveniently produced by thermionic emission from a heated filament. When metals are heated to a sufficiently high temperature, they begin to emit electrons. For most metals, this temperature is quite high of the order of 2000 to 2500°C. By heating the metal, the kinetic energy of some electrons is increased sufficiently to enable them to escape from the metal surface. Since 1 cubic centimeter of gas at atmospheric pressure contains 2.6×10^{19} molecules, the electrons can travel only minute distances before they collide with a gas molecule. If any positive ions are produced at all, they will very rapidly recombine with the electrons to re-form neutral atoms or molecules. To obtain a useful yield of positive ions it is necessary to reduce the gas pressure to below one-millionth of atmospheric pressure. Positive ions in this case are unlikely to collide with either neutral gas atoms or with electrons before they can be separated according to their mass and can be counted. Under conditions of reduced pressure, the probability of an electron ionizing a gas molecule in a collision depends on the number of gas molecules present (proportional to the gas pressure), the nature of the gas molecule (chemical element or compound), and the energy of the electron. The ionizing efficiency is highest for electrons accelerated to between 50 and 150 volts. As the energy of the electrons increases, more than one electron may be removed in a single collision with a neutral molecule.

Charged particles are acted upon by electric and magnetic forces. The effect of these forces can be expressed mathematically in simple fashion.

The velocity v of a charged particle of charge q and mass m which is released at some reference electric potential and is allowed to fall through a potential difference V volt is given by [1]*

$$v = \sqrt{\frac{2qV}{m}} \quad (1)$$

A charged particle moving with constant velocity v through a uniform magnetic field B moves in a circular path of radius R , where [1]

$$R = \frac{1}{B} \sqrt{\frac{2mV}{q}} \quad (2)$$

*Numbers shown in [] represent reference numbers.

These equations are valid only when the charged particle experiences no collisions with other charged or neutral particles. For the positive ions of interest, this is the case when the gas pressure is less than one millionth of atmospheric pressure.

Equations (1) and (2) are the basic relationships used for the design of mass spectrometers. In one type of instrument (time-of-flight) the time required by a group of ions to travel a given fixed distance is measured. The time interval is inversely proportional to the velocity; it is thus proportional to \sqrt{m} for ions of charge q . The number of ions of a given mass is a measure of the concentration of the atomic or molecular species of mass m . Alternatively, one can measure the number of ions which travel along a particular curved path in a magnetic field (magnetic deflection instrument), where the radius of curvature is proportional to \sqrt{m} for ions of charge q . Before surveying the merits and difficulties associated with the various methods of mass analysis, we first discuss the problem how the pressure in the ionization region of a mass spectrometer can be reduced by more than one million times from atmospheric pressure without affecting the ability of the instrument to record changes in gas composition rapidly and accurately.

It has been demonstrated experimentally that the necessary pressure reduction can be accomplished relatively simply by means of a combination of a small bore capillary several feet long pumped by a vacuum pump. At the low-pressure end of the capillary, a small gas sample is fed into the mass spectrometer via a pin-hole leak. The mass spectrometer is pumped by a small auxiliary vacuum pump.

The critical parameter for breath-by-breath analysis is the response time of the vacuum system, in other words, the time required for a change at the inlet of the capillary to be registered by the mass spectrometer sensor. With careful design, this can be as small as 0.3 seconds, which is adequate for present requirements.

The methods of pumping the gas inlet system and the mass spectrometer to cause a sample flow and to reduce the pressure to a level where the mass spectrometer can operate depend on the proposed application. For in-flight monitoring, weight and power are at a premium. Therefore, the use of highly sophisticated pumps is indicated, namely a sorption pump for the capillary and an ion pump for the mass spectrometer. Very briefly, a sorption pump contains a highly porous absorbing agent such as activated charcoal, silica gel or zeolite crystals. When chilled to liquid-nitrogen temperature, a pump of this type can operate for several hours before it saturates. All that is required is a liquid-nitrogen reservoir of sufficient capacity. An ion pump is an electronic device in which gases are pumped by means of an electrical discharge, normally aided by a permanent magnet. It has been known for many years that ionization of gas in the presence of chemically active electrodes is an efficient means of lowering the gas pressure. It occurs in such common electrical devices as fluorescent lamps and neon tubes. The "clean-up" of the gas is due to several processes: (1) gaseous ions collide with internal surfaces and adhere to them; (2) gaseous ions dislodge and vaporize atoms of the electrodes on impact (this

is known as "sputtering"), and the metallic vapor traps some of the gas molecules when it condenses on the walls; (3) gaseous ions combine chemically with the walls and electrodes, or with sputtered electrode material. In recent years, devices in which those processes are deliberately enhanced have been made available commercially and provide an almost ideal method for pumping gases at low pressure with very small power consumption.

In a terrestrial medical laboratory, the restrictions regarding size, weight and power are, of course, far less severe. Therefore, well-established pump types, namely, a mechanical rotary pump and a diffusion pump (both inexpensive and exceptionally reliable for continuous unattended operation) in lieu of sorption pump and ion pump would certainly be acceptable.

As indicated previously, mass spectrometry involves the measurement of a physical quantity (time-of-flight or radius of curvature) which depends only on $\sqrt{m/q}$, where m/q is the mass-to-charge ratio of an ion, expressed in atomic mass units (AMU). The atomic mass unit ($M/e = 1$) corresponds to the mass-to-charge ratio of the atomic hydrogen ion, and the corresponding values of all other ions are close to whole-number multiples of this quantity. In the case of elements whose atomic weight is clearly not a whole number (chlorine, for example, has an atomic weight of 35.46), mass spectrometric analysis shows that they consist of a mixture of two or more chemically identical atomic species or isotopes, whose respective atomic mass numbers are multiples of the atomic mass unit. Each isotope will yield a discrete current peak proportional to its natural abundance (chlorine is composed of 75.5 percent of isotope 35 and 24.5 percent of isotope 37). The peak occurring at the mass equivalent of molecular ions is designated as the parent peak. There are usually additional peaks due to dissociation, multiple ionization, and fragmentation of molecules by the ionizing electrons in the ion source, as well as peaks due to isotopes. The largest peak is called the major peak whether it occurs at the mass equivalent of the parent molecule or not. All peaks which appear from a given substance are called the cracking pattern which is characteristic of the substance. The cracking pattern can be changed by many factors in the ion source, but the fragmentation and multiply-charged ion intensities bear a constant relationship to the parent molecule under constant conditions in a particular instrument. A typical mass spectrogram recorded experimentally with a methane sample (Figure 1) [1] shows the characteristic cracking pattern with major peak at $M/e = 16$. The cracking pattern can also be represented graphically by rectangles whose heights are proportional to the heights of the experimental peaks (Figure 2)[1], or in the form of a table, with the peak heights listed relative to the major peak (Table I), [1]. It is apparent that several different species occupy the same position on the atomic mass scale and, also, that a given mass peak may result from different parent molecules. The relative output signal is a measure of the rate at which positive ions of a particular species are produced in the ion source; the rate of positive ion production, in turn, is proportional to the partial pressure of the parent substance. The constant of proportionality has to be determined by a separate calibration for each gas or vapor. This includes a determination of the magnitude of output signal per unit of pressure, called the sensitivity. Another important characteristic is the resolution of a given instrument. This is defined as the ratio, $M/\Delta M$, where M is the atomic

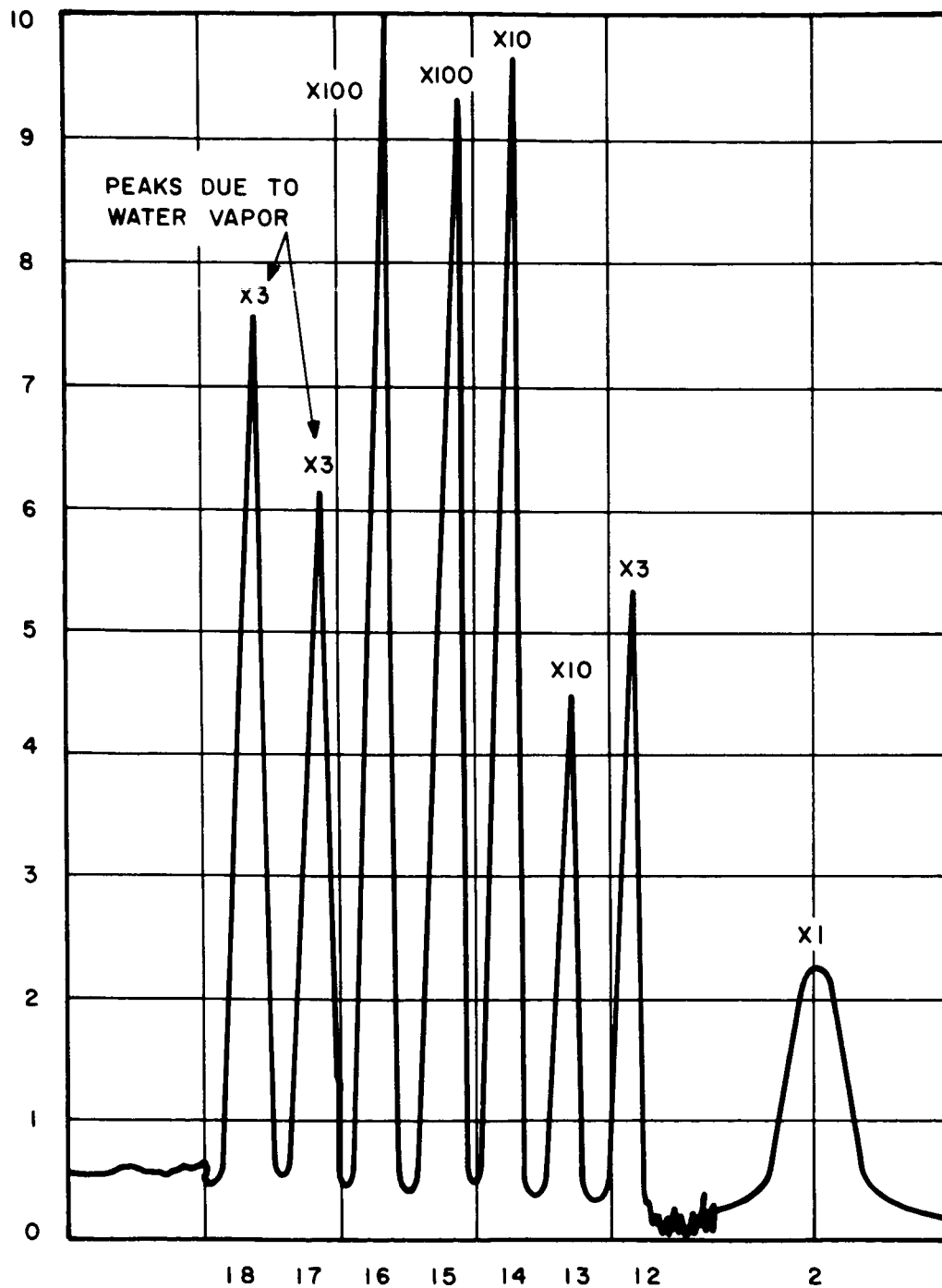


Figure 1. Cracking Pattern of Methane Sample.

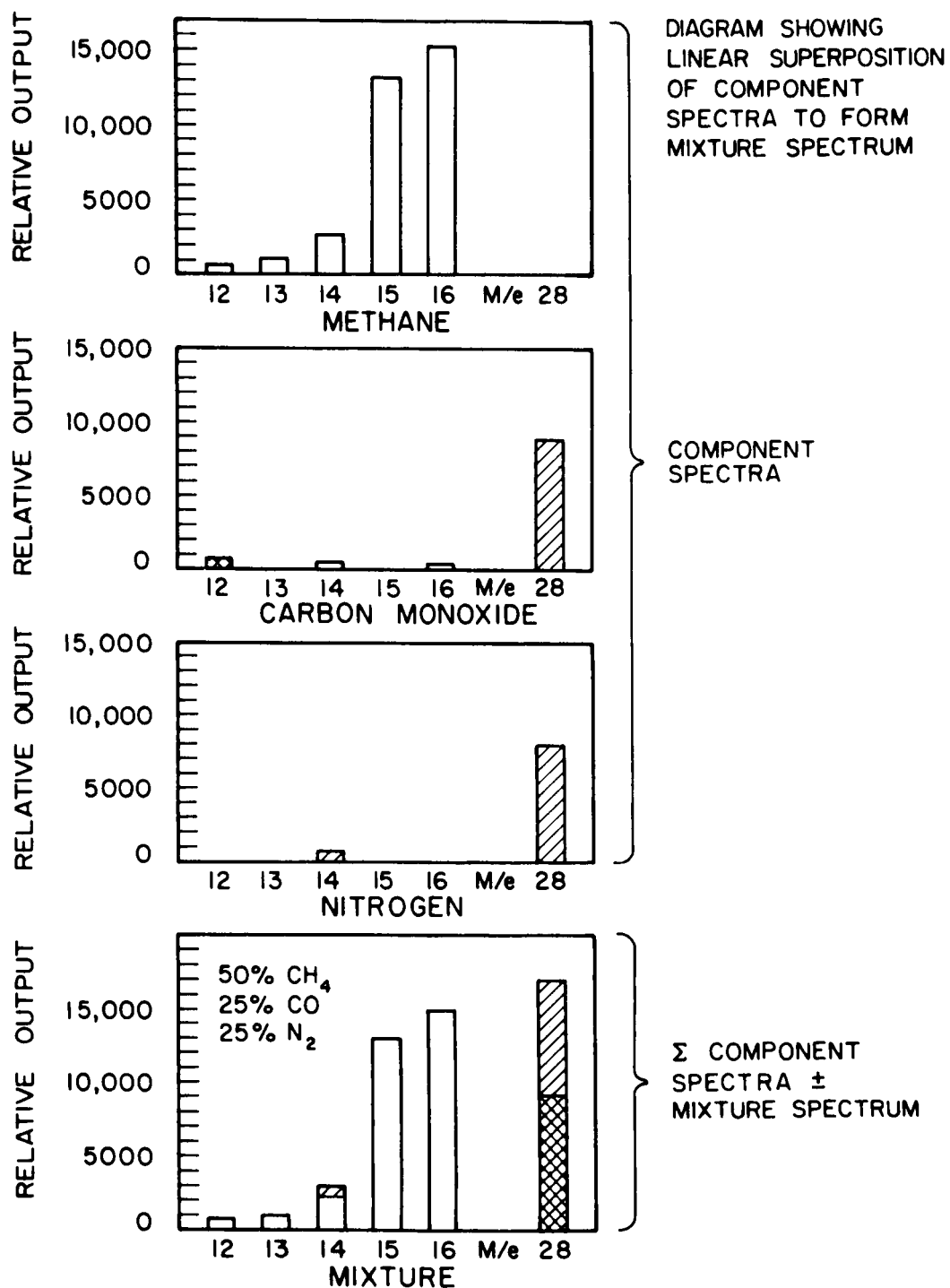


Figure 2. Component spectra and mixture spectrum.

TABLE I

Gas Parent Peak	CH ₄ (methane) 16			H ₂ O (water) 18		
Cracking pattern	M/e	Species	%	M/e	Species	%
	16	CH ₄ ⁺	100	18	HOH ⁺	100
	15	CH ₃ ⁺	80	17	OH ⁺	30
	14	CH ₂ ⁺	12	16	O ⁺	4
	13	CH ⁺	5			
	12	C ⁺	2			
Gas Parent Peak	CO (carbon monoxide) 28			C ₄ H ₁₀ (butane) 58		
Cracking pattern	M/e	Species	%	M/e	Species	%
	30	¹² C ¹⁸ O ⁺	0.2	58	C ₄ H ₁₀ ⁺	12
	29	¹³ C ¹⁶ O ⁺	1.2		C ₂ H ₇ ⁺	100
	28	CO ⁺	100.0	42	C ₃ H ₆ ⁺	13
	16	O ⁺	3.5	41	C ₃ H ₅ ⁺	33
	14	CO ⁺⁺	1.0	39	C ₃ H ₃ ⁺	18
	13	¹³ C ⁺	0.3	29	C ₂ H ₅ ⁺	44
	12	C ⁺	8.5	28	C ₂ H ₄ ⁺	33
				27	C ₂ H ₃ ⁺	44
				26	C ₂ H ₂ ⁺	11
				15	CH ₂ ⁺	10

mass number at which a particular peak occurs, and ΔM is the width, expressed in atomic mass units, of the peak at half amplitude. Depending on the particular use of the instrument, it may be desirable to sacrifice resolution for the sake of sensitivity, and vice versa. In many instruments, resolution is controlled by a system of slits through which the beam of ions reaches the ion collector. By narrowing the slits, discrimination between adjacent mass peak is improved, but the intensity of the ion beam is reduced. Instruments available commercially for the analysis of common gases are usually designed with a resolution of less than 100.

The minimum detectable concentration (partial pressure) of a particular gas in a gas mixture depends on the nature of the mixture, on the required response time and on the quality of the mass analyzer and the associated electronics. Typical values for the present application demonstrated in practice are between 20 parts per million to 1000 parts per million.

When resolution has to be limited to improve sensitivity, difficulties arise in identifying gases whose mass peaks occur at the same mass number. Probably the most common example occurs at 28 AMU, where a peak may be due to the singly-charged nitrogen molecule (N_2^+ = 28.0150 AMU) or the singly-charged carbon monoxide molecule (CO^+ = 28.0039 AMU). Here, a resolution of $28/0.0111 = 2500$ is required, and, therefore, it is not possible to differentiate directly between these two gases with an instrument whose resolution is only 100. It then becomes necessary to examine the spectrum for secondary peaks. As an example, consider a typical instrument which indicates the atomic nitrogen peak (N^+) at 14 AMU as 7.4 percent of the N_2^+ peak and the atomic carbon peak (C^+) at 12 AMU as 3.3 percent of the (CO^+) peak. The doubly-charged carbon monoxide ion (CO^{++}) which appears at 14 AMU is 0.55 percent of the (CO^+) peak. Unless the partial pressure of either gas is high enough for the secondary peaks to be detectable, the spectrum cannot be identified in this manner. Apart from minor difficulties of this nature, however, spectra of the gas mixtures encountered in the present application are not difficult to analyze.

A problem not yet discussed is the accuracy of quantitative chemical analysis. As mentioned previously, the probability of ionization by electron impact depends only on the nature of the gas molecules, when all other factors, such as ionizing electron density and energy, are kept constant. It is possible to perform an absolute separate calibration for each gas of interest. This procedure is laborious and time-consuming and has to be repeated at frequent intervals. It is much simpler to connect a calibration mixture of accurately known composition to the sample inlet and to measure the relative peak heights of the various component molecular ions periodically. By a measurement of this nature, an accuracy of within 10 percent can readily be obtained.

Two practical approaches which have demonstrated the workability of breath-by-breath analysis will now be described.

The time-of-flight scheme is shown in Figure 3, [2]. It consists of the afore-mentioned capillary sample inlet pumped by the sample system pump, the pin-hole or molecular leak through which the gas to be analyzed is admitted

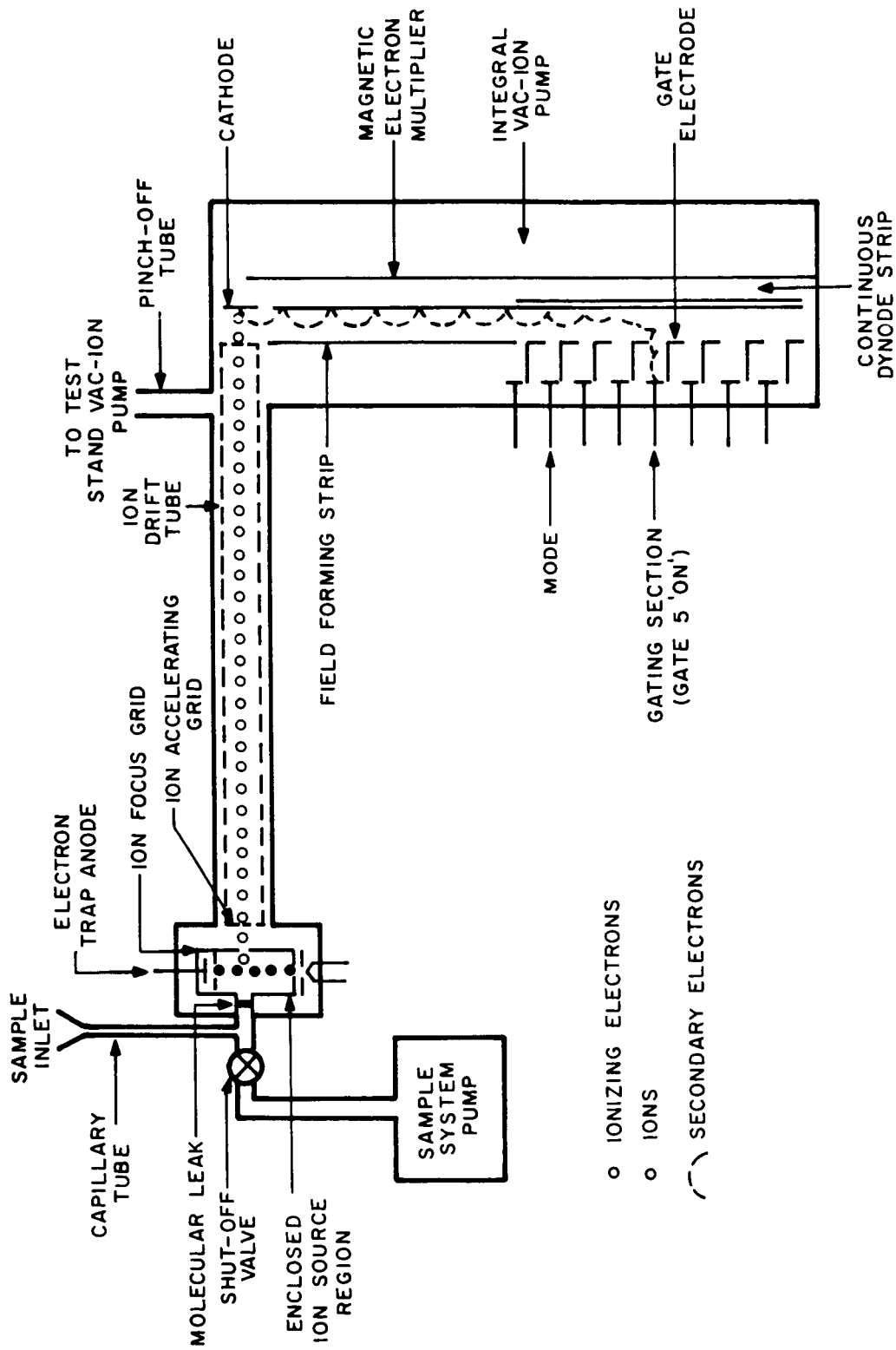


Figure 3. Time-of-Flight Mass Spectrometer System.

into the ion source, the ion drift tube pumped by an ion pump, and an ion detector. This particular detector is called an electron multiplier ions impinging on the first electrode (cathode) release electrons which are directed via a magnetic field onto successive electrodes (continuous dynode strip). If each electron releases additional electrons on bombarding the dynode strip, almost instantaneous internal amplification occurs.

The ion source contains an electron gun in which electrons are produced at a hot filament. The gas sample is ionized by a pulsed electron beam which traverses the ion source region. The electron beam is pulsed for a fraction of a microsecond (one millionth of a second) from the spectrometer master timer which operates at a repetitious rate ten thousand times per second. At the end of the ionizing pulse period, the positive ions produced in the ion source are ejected from the source region by a negative pulse applied to the ion focus grid. In the region between the ion focus grid and the ion accelerating grid, the ions are accelerated by the same electric potential and therefore emerge from the accelerating region with velocities inversely proportional to \sqrt{m} .

Beyond the ion accelerating grid is the ion drift tube; here, the ions separate into bunches according to mass, the separation increasing as the discrete ion bunches progress through the drift tube. The group of ions of lowest mass arrives first at the cathode, followed in succession by ions of heavier mass. The electron multiplier is equipped with a multichannel output gating assembly which permits the multiplier output pulses corresponding to a selected mass peak to be gated onto a selected anode. All other mass peaks in the spectrum will bypass that anode; other mass peaks may, however, be gated onto the anodes of other channels. The gate pulse width of a few nanoseconds (thousandths of one millionth of a second) is slightly greater than the width of a mass peak, so that only one mass peak is collected on each anode. Since the selected mass peak occurs at the same time in each successive spectrum, the anode collects a succession of current pulses corresponding to the selected mass peak. The measured peak height corresponds to the average anode current.

Any mass peaks in the spectrum not gated into one of the output channels impinges on our ungated anode at the end of the multiplier gating region. If none of the spectral peaks are gated, then the entire mass spectrum appears as a succession of pulses on the ungated anode. This spectrum can be viewed with an oscilloscope whose time-sweep is synchronized at the spectrum repetition rate.

It may be concluded that the time-of-flight mass spectrometer sensor is relatively simple mechanically; the associated electronic circuitry is, however, of considerable complexity.

In contrast, the magnetic deflection mass spectrometer sensor is somewhat more complicated mechanically, but presents relatively fewer problems electronically. The schematic in Figure 4 [3], demonstrates the method of operation of the type of instrument constructed for inflight measurements of six constituent gases. On the left side is the ion source with a continuous electron beam

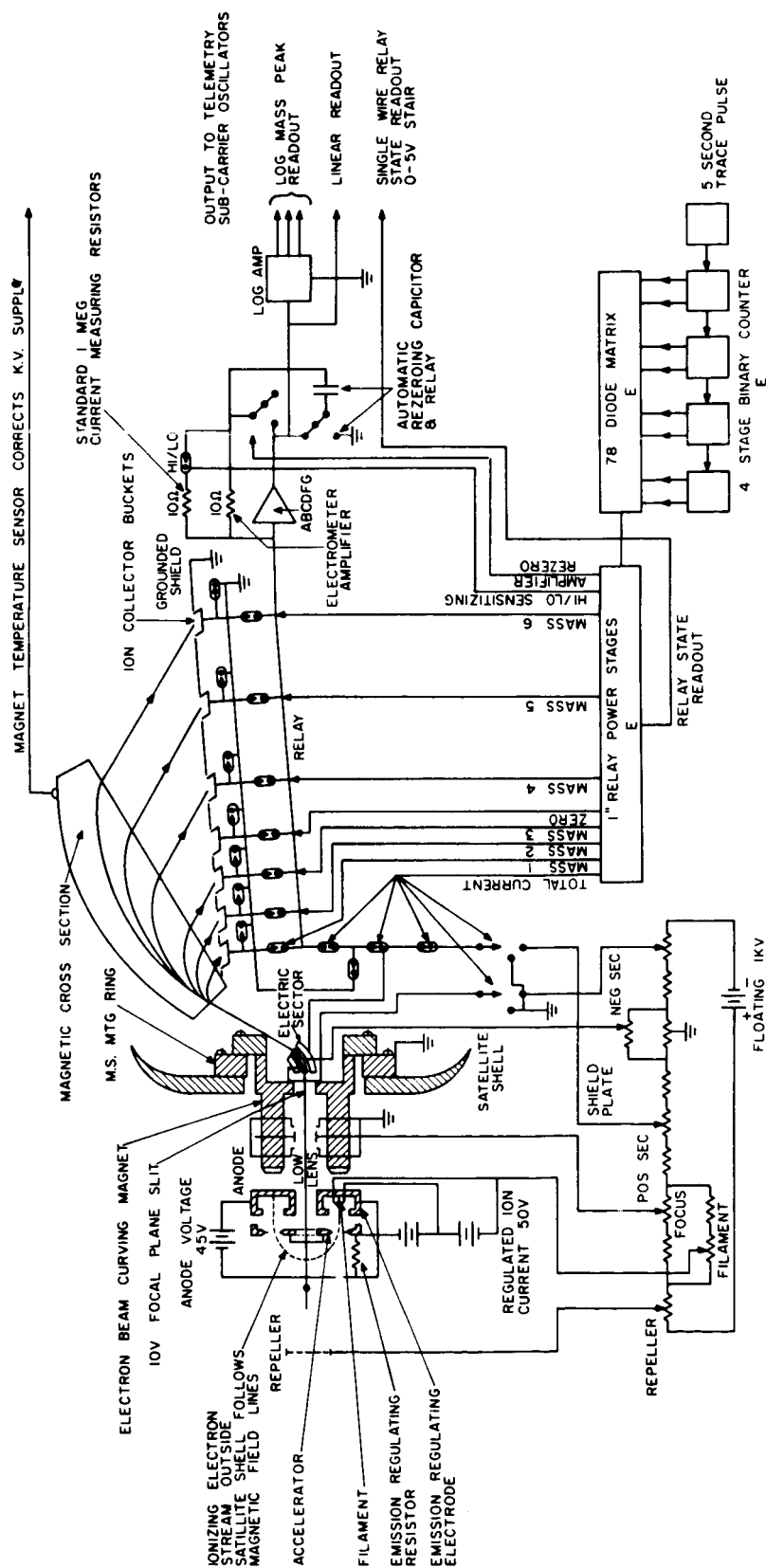


Figure 4. Method of Operation of Magnetic Deflection Mass Spectrometer (Six Gases) Sensor.

traveling between the filament and the anode. From the ionizing region, particles pass through an entrance slit into an electric sector and are separated according to mass in the gap of a permanent magnet. Ions of particular mass follow a path of constant curvature. It is possible to collect such ions by strategically locating a number of ion collector brackets. The ion current to each ion collector can be monitored continuously by electrometer amplifiers whose output can be fed into a strip-chart recorder. The mechanical and electrical tolerances of the mass spectrometer sensor become closer as the number of collector buckets increases. The monitoring of the ion currents, on the otherhand, is less complicated than in the case of the time-of-flight mass spectrometer.

A complete sampling and sensing system for twelve constituent gases, utilizing a magnetic deflection mass spectrometer is shown in Figure 5, [4]. It is designed to monitor H_2 , CO , CH_4 , NH_3 , H_2O , N_2 , COH , O_2 , H_2S , HC , CO_2 and $COOH$. It includes four sample inlet capillaries, a calibration sample, a liquid-nitrogen chilled sorption pump and an electronic ion pump.

Typical breath-by-breath analysis performed with this device is shown in Figure 6, [4] indicating carbon dioxide, oxygen and water vapor constituents. The peak heights are proportional to the concentrations of these gases. It is apparent that this method of display is most suitable for indicating relative changes in concentrations.

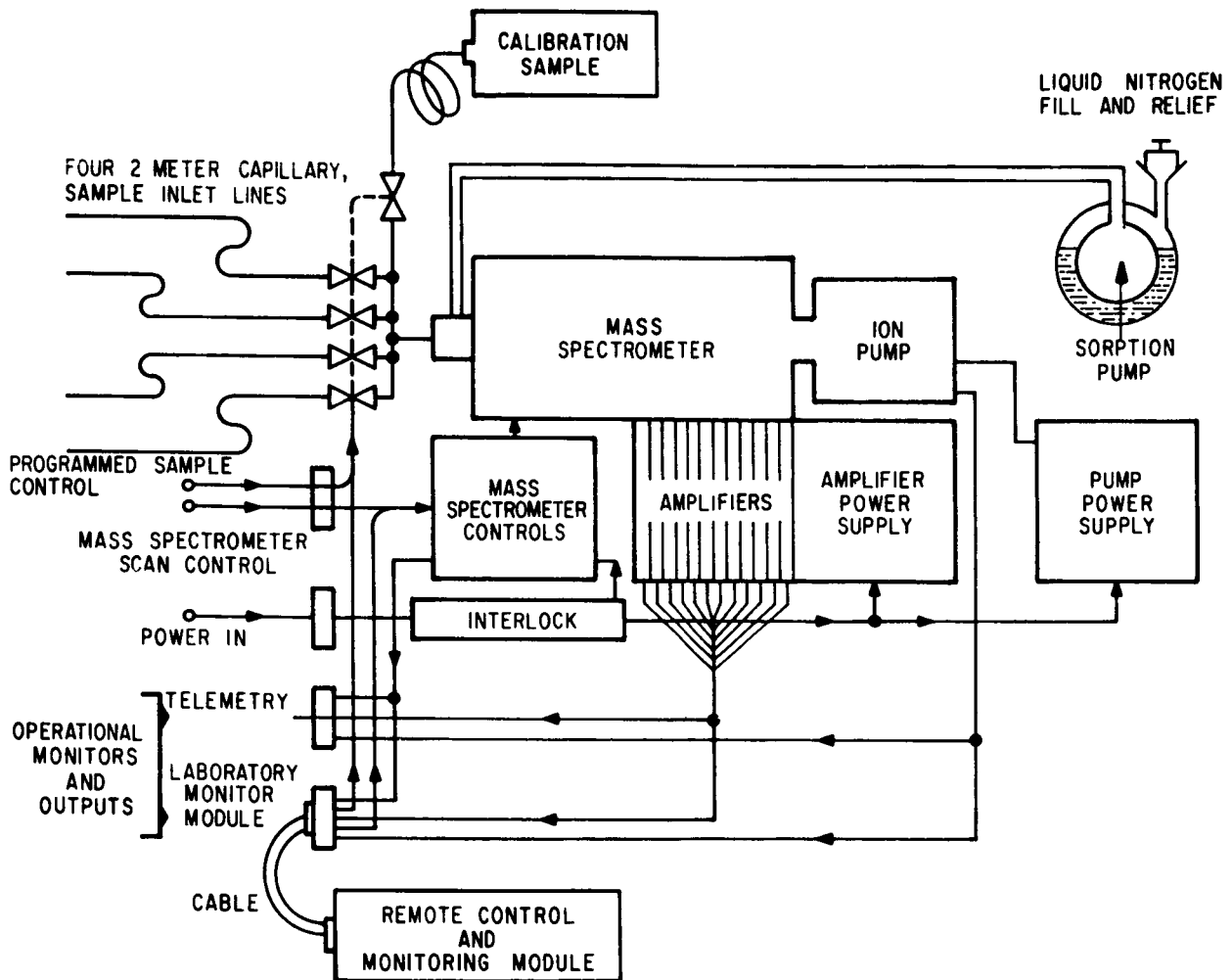


Figure 5. Twelve-gas sampling and sensing system.

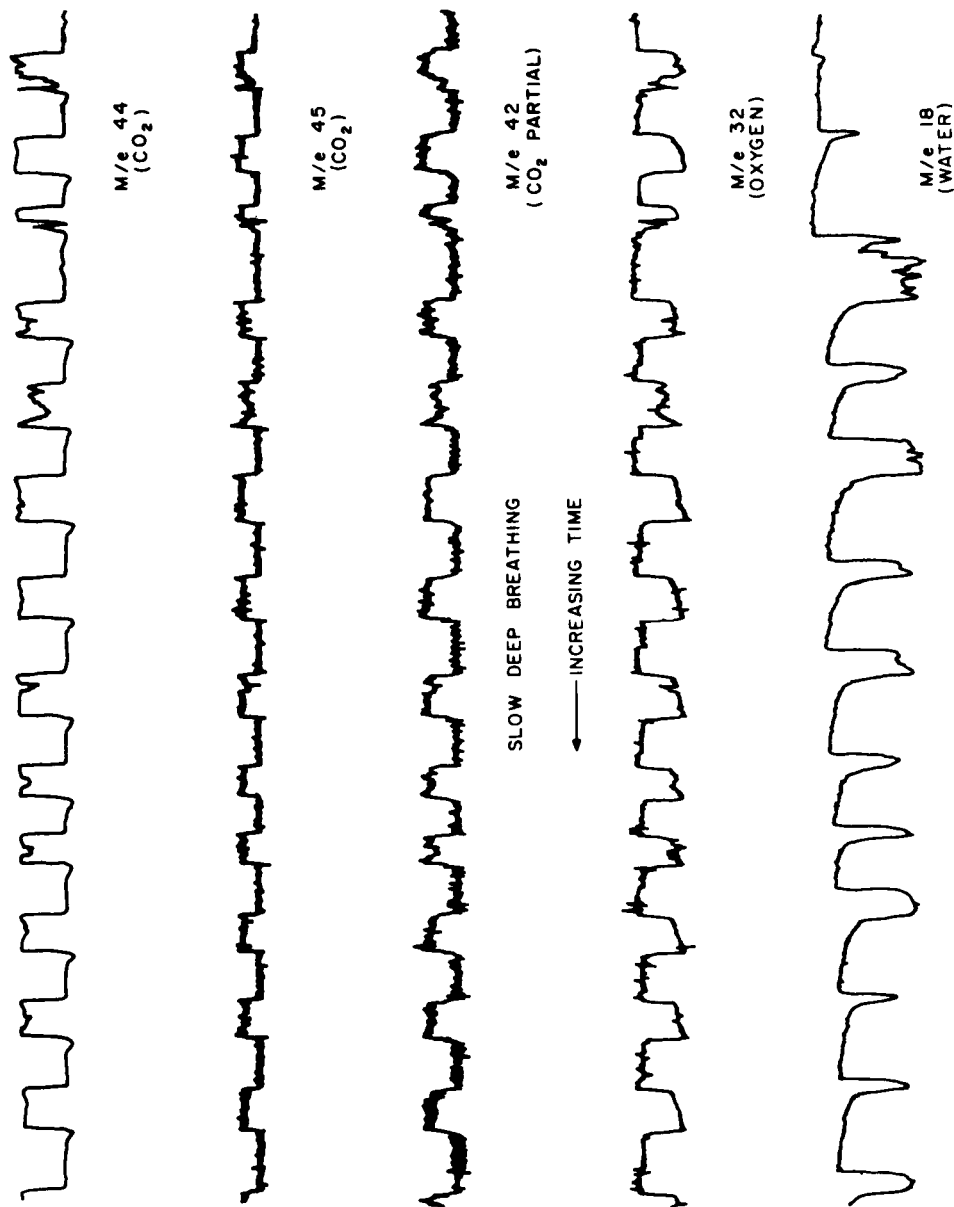


Figure 6. Breath-by-Breath Indication of Expired Constituents.

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